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Planarization of Unsaturated Rings. A Cycloheptatriene with a Planar Seven-Membered Ring

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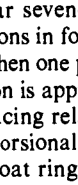
Abstract: Geometrical and structural requirements for the ring planarization of cyclopolyolefins are discussed. As an example, the crystal structure analysis and spectroscopic properties are described for a compound which involves a planar cycloheptatriene ring due to constraining a torsion angle around a C–C single bond at 0°. The constraint is introduced via fusion of a rigid norbornane moiety with the seven-membered ring. Implications for planarizing larger rings, in particular the eight-membered ring of *all-cis*-cyclooctatetraene, are pointed out.

A planar *n*-membered ring has *n* − 3 independent possibilities (normal coordinates) for nonplanar deformations, which may be represented as linear combinations of ring torsion angles. Thus a planar seven-membered ring may be subjected to nonplanar distortions in four different ways. If three torsion angles are fixed at 0°, then one possibility for nonplanar deformation remains. This situation is approximated in *all-cis*-cyclohepta-1,3,5-triene (**1**) by introducing relatively rigid double bonds. The remaining single (soft) torsional degree of freedom in **1** clearly corresponds to the boat–boat ring inversion. The geometrical flexibility properties of **1** may be instructively compared to those of cyclobutane (again one nonplanar deformation possibility corresponding to the ring inversion coordinate) into the four-membered ring of which a cycloheptatriene skeleton with ideally planar, rigid C—C═C—C segments can be inscribed (Figure 1a). Similar considerations are valid for *all-cis*-cycloocta-1,3,5,7-tetraene (**2**) (Figure 1b; see Discussion).[1]

The best structure of cycloheptatriene **1** is a boat conformation with mirror symmetry C_s (Appendix I). According to NMR measurements,[2] the ring inversion of this boat minimum requires an activation energy of 6.3 kcal mol^{-1} and probably proceeds across the planar C_{2v} symmetric form as a transition state. We have been wondering how a system could be structurally realized, the most favorable geometry of which has a planar cycloheptatriene ring. According to the introductory geometrical analysis, for this purpose a ring torsion angle around at least one C–C single bond in **1** is to be fixed at 0°.[3] The respective constraint may be imposed in two ways: (1) fusion of a small ring via a C–C single bond, as for instance in **3** and possibly also in **4** (this measure simultaneously supports planarization through facilitated angle openings in the seven-membered ring which are inevitably required for ring flattening[4]), and (2) fusion of a suitable polycyclic framework via single bonds with sufficiently rigid syn-planar partial conformations, as, for example, in **5**–**7**. Because of angle strain criteria, the known framework **7**[5] appears particularly favorable since also in this example angle openings in the seven-membered ring are relatively easy in view of the compressed C(1)–C(7)–C(4) angle of only 94° in norbornane. (The systems **3**–**6** are unknown.)



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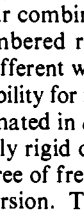

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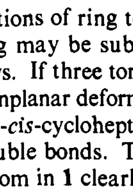

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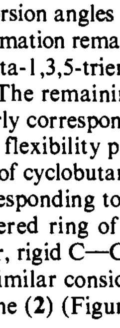

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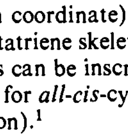

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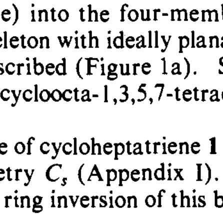

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The question arises as to whether the torsional rigidity of the norbornane skeleton in **7** indeed suffices to planarize the seven-membered ring and whether nonplanar double bond distortions are sufficiently resisted as supposed. A theoretical answer, e.g., with the help of force-field methods, is complicated by the special "homoaromatic" stabilization of the boat minimum of **1**.[6] Therefore, we have attempted an experimental solution of the present structural problem and report here the X-ray analysis of the dicarboxylic acid **8** at room temperature as well as some spectroscopic data. This derivative of **7** is readily available from a diester precursor,[5] and the two carboxylic groups ensure a sufficiently tight molecular packing via hydrogen-bonded chains.

Experimental Section

The *endo,exo*-dicarboxylic acid **8** was prepared by alkaline hydrolysis of the corresponding *endo,endo*- and/or *exo,exo*-dimethyl ester.[5] Apparently, a stereoisomerization occurs under the influence of the base, as evidenced by the subsequent crystal structure analysis.

X-ray Analysis. $C_{14}H_{14}O_4$, M_r 246.3, mp 177 °C, monoclinic crystals from ethyl acetate, space group *Cc* or *C*2/*c* (centrosymmetric choice made), d_x = 1.323 g cm^{-3}, d_m = 1.33 g cm^{-3}, Z = 8, a = 26.146 (19) Å, b = 6.874 (5) Å, c = 13.683 (10) Å, β = 91.49 (7)°, 3580 independent intensities measured at room temperature on a four-circle diffractometer (λ_{Mo} = 0.71069 Å, θ_{max} = 30°), structure solved by direct methods, refinement including the 2920 reflections with $|F_o| > 3\sigma(F_o)$, R = 0.066, R_w = 0.066, all crystallographic calculations performed with the program system SHELX76.

We thank Dr. W. Gebert, Bochum, for the intensity measurements. The refined atomic coordinates and the averaged isotropic temperature factor coefficients are listed in Table I, while Figure 2 shows a stereoview of **8** with vibrational ellipsoids (35% probability), and relevant molecular geometry data, and the atomic numbering. Anisotropic temperature factor coefficients of the heavy atoms and a list of observed and calculated structure amplitudes are available as supplementary material.

Discussion

In the crystals of **8**, the cycloheptatriene ring is practically planar as witnessed by the torsion angles and the sum of the bond

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(1) Similarly, *cis,cis*-cycloocta-1,4-diene and *cis,cis*-cycloocta-1,5-diene may be compared with cyclohexane: Dunitz, J. D.; Waser, J. *J. Am. Chem. Soc.* **1972**, *94*, 5645. It is stressed that these comparisons are geometrical; they do not imply physically (energetically) similar flexibility properties.

(2) Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 458.

(3) For planarization of the seven-membered ring, the fixing of a ring torsion angle at 0° around a C(sp^2)—C(sp^2) single bond is less effective than that around a C(sp^3)—C(sp^2) single bond since in the C_s boat minimum of **1** the C═C—C═C torsion angles are considerably smaller in magnitude than the C═C—C—C torsion angles (Appendix I).

(4) The maximum possible average bond angle in a *n*-membered ring holds for planarity and obviously amounts to 180°(*n* − 2)/*n*, i.e., 900°/7 = 128.57°, in the planar seven-membered ring.

(5) Klärner, F.-G.; Dogan, B.; Roth, W. R.; Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 708; *Angew. Chem. Suppl.* **1982**, 1499.

(6) Lindner, H. J. *Tetrahedron* **1981**, *37*, 535. See also: Roth, W. R.; Böhm, M.; Lennartz, H.-W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1007; *Angew. Chem. Suppl.* **1983**, 1379.

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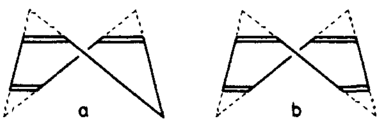

Figure 1. Topological comparison of cyclobutane with (a) cyclohepta-1,3,5-triene (**1**) and (b) cycloocta-1,3,5,7-tetraene (**2**).

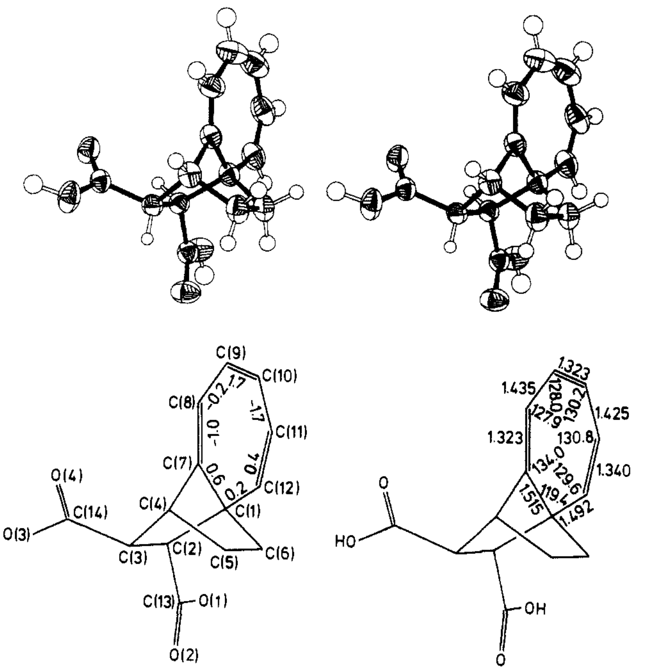

Figure 2. Crystal structure of **8**. (top) Stereoview with vibrational ellipsoids (35%) for the heavy atoms; isotropic temperature coefficients of the H atoms reduced by common factor. (bottom) Atomic numbering and torsion angles (deg; left) and bond lengths and angles (Å, deg; right) in the planar seven-membered ring. Average estimated standard deviations of the lengths, angles, and torsion angles are 0.003 Å, 0.2°, and 0.4°, respectively.

Table I. Fractional Atomic Coordinates [C, O ($\times 10^5$); H ($\times 10^4$)] and Isotropic Temperature Factors [C, O ($\times 10^{4a}$); H ($\times 10^3$)] of **8** with Estimated Standard Deviations in Parentheses

	x	y	z	U_{iso}, Å^2
C(1)	36 548 (6)	55 582 (25)	39 496 (11)	536 (10)
C(2)	37 610 (6)	77 476 (25)	36 555 (10)	487 (9)
C(3)	42 177 (5)	75 825 (25)	29 647 (10)	487 (9)
C(4)	43 099 (6)	53 499 (27)	29 072 (12)	564 (10)
C(5)	45 553 (7)	47 077 (29)	38 812 (14)	671 (11)
C(6)	41 124 (7)	48 516 (28)	45 921 (12)	643 (11)
C(7)	37 764 (6)	45 696 (25)	29 935 (12)	550 (9)
C(8)	35 194 (8)	33 890 (29)	23 957 (15)	719 (12)
C(9)	30 126 (9)	26 296 (35)	25 035 (20)	913 (17)
C(10)	26 951 (8)	29 434 (36)	32 238 (22)	920 (17)
C(11)	27 530 (7)	41 323 (33)	40 730 (17)	788 (14)
C(12)	31 467 (7)	52 276 (30)	43 926 (14)	717 (13)
C(13)	38 647 (6)	90 435 (26)	45 139 (11)	525 (9)
C(14)	41 041 (6)	84 149 (24)	19 682 (11)	507 (9)
O(1)	34 569 (5)	95 210 (21)	49 778 (9)	747 (9)
O(2)	42 939 (5)	95 531 (20)	47 811 (9)	734 (9)
O(3)	45 137 (4)	88 767 (22)	15 031 (9)	772 (9)
O(4)	36 782 (4)	85 937 (20)	16 176 (8)	665 (8)
H(2)	3 455 (5)	8 258 (21)	3 263 (10)	51 (4)
H(3)	4 510 (5)	8 259 (20)	3 199 (9)	45 (4)
H(4)	4 508 (6)	4 870 (24)	2 359 (12)	74 (5)
H(51)	4 657 (6)	3 341 (26)	3 765 (13)	84 (6)
H(52)	4 816 (6)	5 572 (25)	4 073 (12)	73 (5)
H(61)	4 014 (6)	3 604 (23)	4 849 (11)	65 (5)
H(62)	4 171 (6)	5 833 (28)	5 173 (13)	83 (6)
H(8)	3 729 (7)	2 924 (30)	1 816 (14)	95 (6)
H(9)	2 894 (8)	1 858 (35)	1 957 (17)	122 (8)
H(10)	2 398 (8)	2 317 (35)	3 307 (18)	125 (8)
H(11)	2 458 (7)	4 129 (28)	4 472 (14)	90 (6)
H(12)	3 117 (6)	5 896 (27)	5 037 (12)	83 (6)
H_{ox}(1)	3 518 (9)	10 160 (35)	5 444 (18)	133 (8)
H_{ox}(3)	4 454 (8)	9 536 (30)	877 (15)	109 (7)

[a] For C and O equivalent isotropic temperature factors $U_{eq} = {}^1/_3\sum_{i=1}^{3}U_{ii}$ are listed.

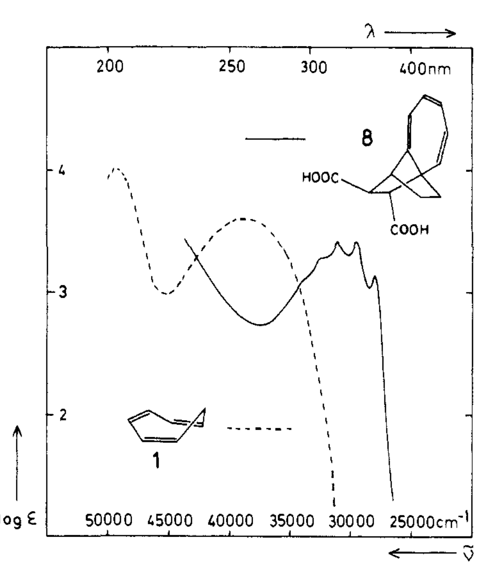

Figure 3. UV spectra of **8** and cycloheptatriene **1** (95% EtOH; room temperature; individual maxima of the vibrationally structured π,π^* band of **8** at 307, 321, 337, and 356 nm).

angles (899.97°) in the seven-membered ring (Figure 2; angle sum 900° for exact planarity[4]). Therefore, the seven-membered-ring angles are widened as compared to standard values, expectedly most pronounced at C(7) since the norbornane angle C(1)–C(7)–C(4) is distinctly compressed (see above). The bond lengths in the seven-membered ring are normal, apart from slight shortenings of the C(sp^2)–C(sp^2) single bonds[7] which, however, cannot be attributed too high a weight due to the relatively large temperature motion of the carbon atoms involved (Table I, Figure 2).[9] From the bond length pattern of the seven-membered ring in **8** no compelling evidence may be gleaned in favor of a "pseudoaromatic" stabilization of the planar cycloheptatriene system as envisaged for planar **1** by Doering et al. 30 years ago;[10] a low-temperature X-ray measurement would be desirable. Recent quantum-chemical computational evidence is in accord with this conclusion.[11] The smallness of the pseudoaromatic stabilization of **7** (and thus also of planar **1**) is a consequence of the rather large distance between the double bond carbon atoms linked to the C(sp^3) atom in the seven-membered ring, which is also related to the angle openings ensuing from the planarization. The distance C(7)···C(12) observed in **8** amounts to 2.597 (3) Å with the angle C(7)–C(1)–C(12) opened by about 10° relative to the tetrahedral

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(7) For comparison, the C(sp^2)–C(sp^2) single bond lengths (gas-phase electron diffraction) of the following olefins are given: *trans*-hexatriene 1.457 (2) Å,[8a] *cis*-hexatriene 1.462 (2) Å,[8b] 1,3-cyclohexadiene 1.465 (2) Å,[8c] 1.468 Å,[8d] 1.468 (14) Å,[8e] 1,3-butadiene 1.467 (1) Å.[8f]

(8) (a) Traetteberg, M. *Acta Chem. Scand.* **1968**, *22*, 628. (b) Traetteberg, M. *Acta Chem. Scand.* **1968**, *22*, 2294. (c) Traetteberg, M. *Acta Chem. Scand.* **1968**, *22*, 2305. (d) Dallinga, G.; Toneman, L. H. *J. Mol. Struct.* **1967**, *1*, 11. (e) Oberhammer, H.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 10. (f) Haugen, W.; Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1726.

(9) The anisotropic temperature motion of the carbon atoms of the framework made up by C(1) to C(12) may be interpreted by a rigid-body model with only fair agreement. The CC lengths of the seven-membered ring corrected for libration result on the average 0.006 Å longer than the uncorrected values shown in Figure 2.

(10) Doering, W. v. R.; Laber, G.; Vonderwahl, R.; Chamberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448. For a related discussion, see also: Evans, M. V.; Lord, R. C. *J. Am. Chem. Soc.* **1960**, *82*, 1876. As is well-known, the assumption made here of a planar seven-membered ring for the preferred structure of cycloheptatriene could not be upheld for long (Appendix I).[2,12]

(11) Cremer, D.; Dick, B.; Christen, D. THEOCHEM **1984**, *110*, 277.

value (Figure 2). In the boat minimum of **1** the analogous distance is about 0.2 Å shorter[12] (Appendix I).

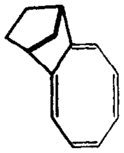
The crystal structure analysis of **8** thus shows that the torsional resistance around the bond C(1)–C(7) in the norbornane skeleton is sufficient to enforce planarity of a cycloheptatriene ring fused via this bond. In the same sense, the double bonds of the seven-membered ring are rigid enough with respect to nonplanar deformations. This evidence provides good experimental support, although no rigorous proof, for the assumption that the transition state of the ring inversion of cycloheptatriene **1** indeed possesses a planar seven-membered ring. Justification of this conclusion simply derives from the fact that the introduction of the minimally required geometric constraint, i.e., a ring torsion angle around just one C–C single bond that passes through 0°, apparently leads to planarity of the whole seven-membered ring.[13]

Expectedly, the π,π^* band in the UV spectrum of **8** centered at around 320 nm is substantially shifted toward longer wavelengths compared to that of nonplanar cycloheptatriene **1** (λ_{max} = 258 nm, Figure 3) and 1,7,7-trimethylcycloheptatriene (λ_{max} = 278 nm; 95% EtOH in all three cases). From the magnitude of this bathochromic shift again no clear evidence supporting special pseudoaromatic effects in planar cycloheptatriene may be derived. It is noteworthy that the π,π^* band of **8** shows vibrational structure, whereas that of **1** does not (Figure 3). This observation allows the conclusion that the planar seven-membered ring in **8** is indeed rather rigid, whereas the soft torsional (inversion) potential of cycloheptatriene **1** leads to a quenching of the vibrational structure.

Another spectroscopic manifestation of the planarization of the seven-membered ring in **8** concerns the chemical shift of H(12) in the ^{1}H NMR spectrum, which is about 1 ppm larger than that of H(6) in 1,7,7-trimethylcycloheptatriene (5.95 vs. 5.1–4.8 ppm) and other substituted cycloheptatrienes. This difference may be readily explained by a shielding effect of the double bond C(1)=C(2) in the nonplanar cycloheptatrienes.

We conclude this report with some considerations as to the planarization of larger cyclopolyenic rings, in particular the eight-membered ring of cyclooctatetraene **2**. The discussion is mainly of geometrical nature, and we shall not speculate about the issue of chemical synthetic feasibility and stability. If systems of the type presented would indeed prove makable and reasonably stable, they would represent rather attractive molecular models for the experimental study of intriguing structural, energetic, and spectroscopic properties related to concepts of aromaticity and antiaromaticity.

Five torsion angles are to be fixed at 0° for planarization of an eight-membered ring. *all-cis*-Cyclooctatetraene **2** with synplanar C—C=C—C torsion angles and one C=C—C=C torsion angle fixed at 0° is therefore planar according to the geometric necessities pointed out in the Introduction. Planar **2** of symmetry D_{4h} (localized double bonds) may be estimated from NMR data (of suitable derivatives) to be about 10 kcal mol^{-1} less stable than the boat minimum (D_{2d}), provided the ring inversion of **2** proceeds across the planar D_{4h} structure as a transition state[14] (Appendix II). Expectedly, this inversion barrier is higher than that of cycloheptatriene **1** since the planarization of **2** requires average angle openings to $^6/_8 180°$ = 135°.[4] On the other hand, the inversion barrier of **2** is still small enough such that ring planarization appears again feasible by fusion of suitable rigid bicyclic frameworks or small rings via C–C single bonds. The relative rigidity of the planar seven-membered ring in **8** following from the UV spectrum (see above) supports this expectation. Favorable hypothetical examples are **9**, **10**, and **11**, possibly also **12**.[15] In addition to the torsional constraint, the planarization of the eight-membered ring is facilitated particularly in **11** since the CCC angles exocyclic with respect to the three-membered ring have large preferred values of about 150°. (According to an X-ray analysis, a cyclooctatetraene with four fused fluorinated cyclobutane rings has a planar eight-membered ring with the double bonds tending toward localization in the four-membered rings.[16]) In order to avoid that the eight-membered ring escapes planarization by cyclic double bond shifts, the introduction of a second torsional constraint is indicated, preferentially such that equivalent (Kekulé) valence isomers arise ([*a*,*d*]-condensations). The resulting hypothetical systems **13–15** (and possibly also **16**) would be highly attractive target molecules for the experimental study of the antiaromatic properties of planar cyclootatetraene, in particular as regards structures, chemical shifts of the vinylic protons, electronic spectra (UV and PE spectra), and bond-shift barriers (Appendix II). If, for example, **13** could indeed be proven to possess a planar eight-membered ring, this would lend support to the assumption of a planar D_{4h} transition state for the ring inversion of **2**, similar as concluded above for cycloheptatriene **1**.[13] That **15** very likely has a planar eight-membered ring may be inferred from a recent crystal structure analysis of a derivative of dibenzo[*a*,*e*]dicyclopropa[*c*,*g*]cyclooctene[17] possessing this feature.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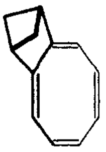
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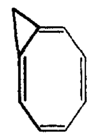
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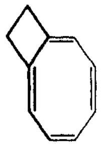
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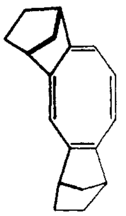
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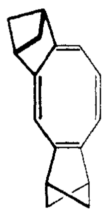
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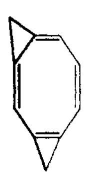
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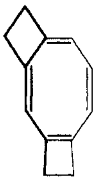
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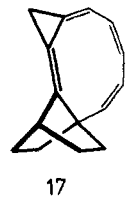
Planarization of the nine- and ten-membered rings of the all-cis isomers of cyclononatetraene and cyclodecapentaene requires fixing two single bond torsion angles at 0° while keeping the double bonds planar (geometrical flexibility relationship with cyclopentane). Since large average ring angle openings out to $^7/_9 180°$ = 140° and $^8/_{10} 180°$ = 144°, respectively,[4] have to be overcome, fusion of three-membered rings would be favorable. Two hypothetical examples interesting in this context would be **17** and **18**.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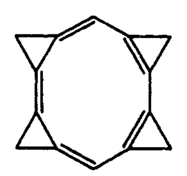
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(12) (a) Butcher, S. S. *J. Chem. Phys.* **1965**, *42*, 1830. (b) Davis, R. E.; Tulinsky, A. *Tetrahedron Lett.* **1962**, 839. Stegemann, J.; Lindner, H. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2161; **1980**, *B36*, 2363. (c) Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265. See, however, the critical comments in Appendix I as regards this gas-phase electron diffraction analysis.

(13) Although unlikely, it cannot be rigorously excluded that the planar C_{2v} and D_{4h} stationary points of **1** and **2**, respectively, actually correspond to intermediate minima on the ring inversion paths. The successful planarization by introduction of the torsional constraints as discussed here would then at least suggest that the inversions of **1** and **2** proceed via planar ring conformations.

(14) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576. Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987.

(15) System **12** is known (Elix, J. A.; Sargent, M. V.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 180; **1970**, *92*, 969) yet probably prefers the valence isomeric structure with single and double bonds shifted within the eight-membered ring such that the four-membered ring is fused via a double bond. The torsional constraints of such a structure are not sufficient for planarization, and the best geometry is likely to correspond to a nonplanar yet flattened eight-membered-ring boat conformation.

(16) Einstein, F. W. B.; Willis, A. C.; Cullen, W. R.; Soulen, R. L. *J. Chem. Soc., Chem. Commun.* **1981**, 526.

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Conclusion

This account serves as an example that purely geometric reasoning may lead to rather intriguing implications as regards the design of model compounds for studying interesting aspects of chemical bonding and structure.

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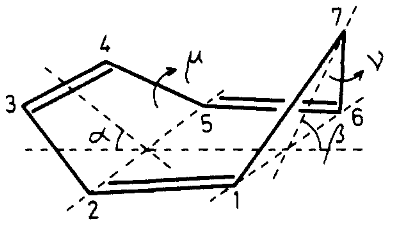
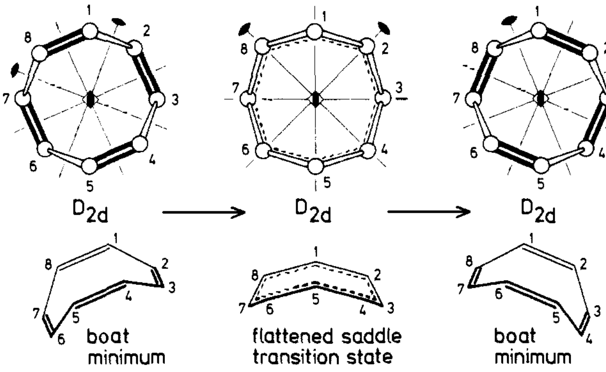
Appendix I. Boat Conformation of Cycloheptatriene 1

The ring puckering of the boat form of **1** may be conveniently described in terms of either the torsion angles C=C—C=C (μ) and C=C—C—C (ν) or the dihedral angles α and β defined graphically below. The torsion angles μ are considerably smaller in magnitude than ν, and similarly $\alpha < \beta$. From a gas-phase microwave measurement of **1**, α and β values of 30 (4)° and 50 (5)°, respectively, have been estimated[12a] ($\mu = -35°$, $\nu = 64°$). Crystal structure analyses of three tri- and tetrasubstituted derivatives of **1** gave α angles between 24° and 37° (μ between -30° and -44°) and β angles between 50° and 53°[12b] (ν between 65° and 66°). On the other hand, the values 41 (2)° and 37 (2)° have been derived by Traetteberg for α and β, respectively, from a gas-phase electron diffraction measurement[12c] ($\mu = -54°$, $\nu = 44°$). As to this contradictory evidence, the following comments are in place: Simple inspection of a molecular model of the C_s boat minimum of **1** shows that within reasonable bond lengths and angles sizable nonplanar deformations of the double bonds C(1)=C(2) and C(5)=C(6) can only be avoided if α is chosen distinctly smaller than β. (Furthermore, decreasing α leads to an energetically favorable enhanced coplanarity of the three double bonds in **1**; the associated angle openings are small.) Accordingly, from Traetteberg's electron diffraction results with relatively similar α and β values the torsion angles C(4)—C(5)=C(6)—C(7) and C(7)—C(1)=C(2)—C(3) are calculated as 23° and -23°! Such large deviation of these double bonds from planarity is hardly tolerable, and a renewed electron diffraction measurement of cycloheptatriene **1** appears indicated. (The boat conformations of the other experimental structure analyses[12a,b] mentioned have planar or nearly planar double bonds.) Even the crystal structure analysis of a *simple* derivative would already allow valuable conclusions to be drawn as regards a more reliable quantitative description of the geometry of the boat minimum of **1**. It is noted finally that recent quantum-chemical calculations[11] also indicate α to be distinctly smaller than β.



Appendix II. Bond-Shift and Inversion Processes of Cyclooctatetraene 2

The bond-shift process (cyclic shift of single and double bonds) of cyclooctatetraene **2** proceeds across a barrier about 4 kcal mol^{-1} higher than the 10 kcal mol^{-1} barrier of the conformational inversion process of **2**.[14] A planar D_{8h} geometry with equivalent CC bonds has been discussed for the bond-shift transition state.[14,18] However, this is little more than mere speculation and is not easy to understand in terms of the associated potential energy surface since the second-derivative matrix of force constants of the D_{8h} stationary point should have more negative eigenvalues than the single one required for a transition state linking two equivalent nonplanar boat minima of **2**, e.g., an additional negative one for in-plane distortion toward the optimal D_{4h} structure with localized double bonds, which is a sensible candidate for the inversion transition state. (The D_{8h} form could in principle also be an intermediate minimum, yet this is a rather unlikely possibility.) A more reasonable alternative would be that the D_{8h} structure is actually a three-dimensional partial maximum on the potential energy surface with one negative eigenvalue for in-plane distortion (a B_{1g} mode) toward the D_{4h} inversion transition state and two negative (degenerate) eigenvalues for out-of-plane deformations (E_{2u}) toward the D_{2d} boat minimum and a (flattened) saddle-shaped transition state also of D_{2d} symmetry (mirror planes through two pairs of opposite ring atoms), which interconvert along a path of hindered pseudorotation under conservation of S_4 symmetry. This pseudorotational coordinate would then correspond to the minimum-energy path of the bond-shift process of **2**. The flattened saddle conformation of D_{2d} symmetry suggested here as a transition state for the bond-shift process of **2** appears sensible also inasmuch as its CC lengths are equal by symmetry, like in the energetically less favorable D_{8h} structure. (The term "saddle" is used here as a pictorial conformational descriptor; its correspondence with a "saddle point", i.e., a transition state, on the potential energy surface is nice yet only accidental. Although not very likely, the D_{2d} saddle conformation could in principle also correspond to an intermediate minimum on the pseudorotational coordinate, yet such that this whole path is energetically below the D_{8h} maximum.) Should, for example, the system **13** be makable, be amenable to physical measurements, and prove to possess a planar eight-membered ring, then possibly some conclusions could be drawn as to the geometry of the bond-shift transition state of **2**: the bond-shift barrier of **13** would be expected to be around 4 kcal mol^{-1} if the respective barrier of **2** would correspond to a planar D_{8h} geometry; a bond-shift barrier of **13** larger than 4 kcal mol^{-1} would hint at a nonplanar respective transition state of **2** with a flattened saddle conformation of D_{2d} symmetry as a good candidate.



Some time ago, a nonplanar crown conformation of D_{4d} symmetry has been discussed as a transition state for the bond-shift process of cyclooctatetraene **2**.[19] However, this suggestion is difficult to reconcile with symmetry and qualitative energy considerations and does not appear very convincing. With a good quantum-mechanical model, the calculation and diagonalization of the force-constant matrices of the D_{8h}, D_{4h}, D_{2d} (flattened saddle), and D_{4d} stationary point conformations of **2** would be highly desirable in order to gain further quantitative insight into the inversion and bond-shift mechanisms.

Registry No. 8, 102922-04-3.

Supplementary Material Available: Anisotropic temperature factor coefficients of the carbon and oxygen atoms of **8** and a list of observed and calculated X-ray structure amplitudes (13 pages). Ordering information is given on any current masthead page.

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